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THE OZONE DEPLETION POTENTIALS ON HALOCARBONS: THEIR DEPENDENCE OF CALCULATION ASSUMPTIONS

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ABSTRACT

The concept of Ozone Depletion Potential (ODP) is widely used in the evaluation of numerous of halocarbons and of their replacements effects on ozone, but the methods, assumptions and conditions used in ODP calculations have not been analyzed adequately.

In this paper a model study of effects on ozone of the instantaneous releases of various amounts of CH_3CCl_3 and of CHF_2Cl (HCFC-22) for several compositions of the background atmosphere are presented, aimed to understand the connections of ODP values with the assumptions used in their calculations.

To facilitate the ODP computation in numerous versions for the long time periods after their releases, the above rather short-lived gases and the one-dimensional radiative photochemical model of the global annually averaged atmospheric layer up to 50 km height are used.

The variation of released gas global mass from 1 Mt to 1 Gt leads to ODP value increase with its stabilization close to the upper bound of this range in the contemporary atmosphere. The same variations are analyzed for conditions of the CFC-free atmosphere of 1960-ies and for anthropogenically loaded atmosphere in the 21st century according to the known IPCC "business as usual" scenario. Recommendations for proper ways of ODP calculations are proposed for practically important cases.

1. INTRODUCTION

Since D.Wuebbles [1983] suggested to use the Ozone Depletion Potential (ODP) of a gas as the measure of its impact on ozone, many publications have been devoted to the ODP calculation problem and to the ODP based recommendations for the replacement of the chlorofluorocarbons (CFCs) by the less dangerous for ozone compounds (e.g. hydrochlorofluorocarbons (HCFCs)), reviewed in [WMO,1989; WMO/UNEP,1991].

The simplicity of ODP physical interpretation and its clarity leads to wide use of this concept by non-specialists and to its introduction into such important international treaties as the Montreal Protocol and some other regulations [WMO,1988]. Such ODPs universality causes the need to estimate the precision of ODP calculations and its sensitivity to the assumptions used in the model and on conditions of the experiment.

For the definition of ODP of compound A:

a). the background steady state atmospheric composition is selected;

b). the prescribed instantaneous release of compound A is modelled;

c). the atmospheric composition change calculations are continued up to the moment when the initial background atmospheric composition is restored (infinite long by the theory);

d). the calculated total ozone changes $\Delta X(t)$ are time integrated (to infinity also by the theory);

e). the a)-d) steps are repeated for CFC-11 as for compound A;

f). the ODP of compound A is the ratio of obtained in item d) integral to similar integral for CFC-11 according to the following mathematical expression:

$$ODP(A) = \frac{\int_0^\infty \Delta X_A(t)\,dt / \Pi(A)}{\int_0^\infty \Delta X_{CFC\text{-}11}(t)\,dt / \Pi(CFC\text{-}11)},$$

where $\Pi(A)$ and $\Pi(CFC\text{-}11)$ are the compound A and CFC-11 fluxes (releases) into the atmosphere (in mass units).

Since the atmospheric photochemical processes are essentially non-linear and the intensive anthropogenic pollution of the global atmosphere occurs, it is evident that:

a). the ODP value of compound A essentially depends on the initial background atmospheric composition (this suggestion is confirmed by S.Solomon et al. [1992], who with aid of modelling and observed data revealed the ODP dependence on the latitude of A injection);

b). the ODP value may depend on the scale of the A modelled release;

c). the total ozone changes in the atmosphere affected by instantaneous release are not equivalent to the total ozone changes in the continuously affected (more close to reality) atmosphere.

In this paper ODP sensitivity to the background atmospheric composition and to the compound release scale is investigated. The methylchloroform (CH_3CCl_3) and HCFC-22 (CHF_2Cl) are selected as considered compounds, as they have relative short lifetimes and this circumstance allows one to reduce the computer time required for calculations of numerous variants. Consequently the ratio RDP=ODP(CH_3CCl_3)/ODP(CHF_2Cl) instead of the ODP(CH_3CCl_3) and ODP(CHF_2Cl) values is considered.

The calculated variants are presented in the Table 1. Three variants of the steady state background atmospheric composition are considered:

P(past),corresponding to 1967 gas composition (with Cl_y at 40 km equal 0.65 ppbv);

R(recent),corresponding to 1985 gas composition (with Cl_y at 40 km equal 3.02 ppbv);

F(future),corresponding to 2025 gas composition (with Cl_y at 40 km equal 4.15 ppbv), the 2025 gas composition was calculated according to "business as usual" (BAU) IPCC scenario [1992 IPCC Supplement].

The four scales of release are considered for each variant,as indicated at the Table 1. Such range of release masses ensures the estimation of sensitivity and suppression of model "noise" influence on the calculation results.

Table 1. The calculated variants and their parameters.

Initial background atmospheric composition		Annual mass release (in Mt/yr)			
Year	$(Cl_y)_{40}$,ppbv	1.0	17	180	1800
1967	0.65	P1	P2	P3	P4
1985	3.02	R1	R2	R3	R4
2025	4.15	F1	F2	F3	F4
1985-2050	-	-	-	FD3	-

In addition to the steady state variants P,R and F the "dynamic" variant FD3 with continuous changes of atmospheric gas composition in the 1985-2050 period is considered also. The release scale in variant FD3 (180 Mt/yr) allows to obtain the significant effect in spite of the model "noise". The trace gases emissions in variant FD3 is adopted according to BAU IPCC scenario (its 1992 version [1992 IPCC Supplement]). The total ozone change in this variant is the difference between the total ozone deviations in BAU IPCC scenario with and without account of the compound A instantaneous release.

The calculation results have to be considered as the illustration of the system sensitivity to the transient atmospheric photochemistry only. The BAU IPCC scenario is chosen as the most "intensive" and investigated of the known proposed scenarios.

As the qualitative conclusions are the most important, the economically feasible 1-D radiative photochemical model of the annually averaged global atmosphere is used. This model was successfully compared with the known 1-D LLNL model.

The radiative photochemical model is a combination of the 1-D photochemical model and of the radiative-convective model. The model extends from the Earth's surface to the 50 km with 2 km vertical coordinate differences. In the photochemical block 141 gasphase reactions (including 35 photodissociations) among the 42 compounds of the oxygen, nitrogen, hydrogen, carbon, chlorine and bromine groups in the atmosphere are considered; the photochemical equilibrium is assumed for the 20 short-lived compounds. H_2O is calculated in the stratosphere only, in the troposphere relative humidity is assumed to be constant.

In the radiative-convective model the radiation absorption of CO_2, H_2O, O_3, CH_4, N_2O, NO_2, HNO_3, CFC-11 and CFC-12 is considered.

2. THE RESULTS OF MODEL CALCULATIONS

The ratios RDP=ODP(CH_3CCl_3)/ODP(CHF_2Cl) for variants R1-R4 calculated for the finite period of time T in integrals in ODP definition and their dependence on T are presented in Fig.1. The RDP for the t=50 years reaches to 2.01, 2.63 and 2.24 for variants R2, R3 and R4 respectively. It is necessary to emphasize that RDP value change is not linear with the instantaneous release volume increase: its maximum occurs for R3 variant with the common changes of RDP values in about 30%, but this statistics is non - sufficient for the final conclusion. The smallest release of odd chlorine Cl_y in variant R1 is small and its signal is lost in model "noises". Therefore the RDP=0.71 value for this variant is not significant and not correct.

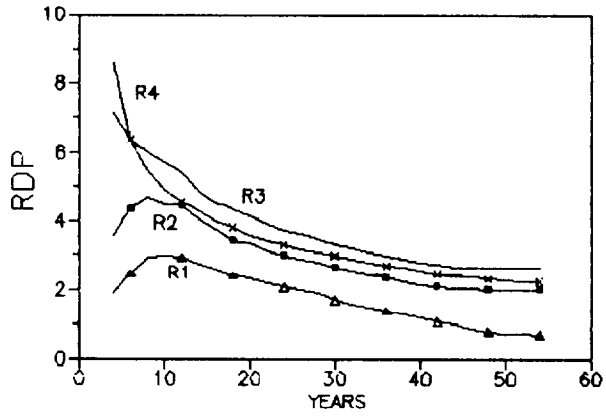

Fig. 1. The time dependence of RDP values for variants R1, R2, R3 and R4 of Table 1.

The Cl_y mixing ratio at 40 km level is maximal at 9-11th model year for CH_3CCl_3 and at 12-14th model year for CHF_2Cl. The maximal values of the Cl_y mixing ratio at 40 km are presented in Table 2.

The similar RDP value is shown in the Fig.2 for variants P2, R2 and F2 (i.e. with the same

Table 2. The maximal values of the Cl_X mixing ratio at 40 km (ppbv) for several variants of Table 1.

Gas	CH_3CCl_3					
Variant	P2	R1	R2	R3	R4	F2
$(Cl_X)_{40}$	1.98	3.09	4.08	14.3	139	5.04
Gas	CHF_2Cl					
Variant	P2	R1	R2	R3	R4	F2
$(Cl_X)_{40}$	1.14	3.05	3.49	7.72	51.4	4.55

release of 17 Mt/yr). The largest RDP value occurs in the "non-freons" atmosphere (variant P). The values of other variants coincide after 10^{th} model year.

The above estimates agree well with ODP values presented in [WMO,1989] and obtained by use of various models. The RDP value changes from 2.0 to 3.2 according to different models. For example:

RDP=0.16/0.05=3.2 (2-D OSLO model),
RDP=0.15/0.05=3.0 (2-D LLNL model),
RDP=0.18/0.06=3.0 (2-D AER model),
RDP=(0.1-0.13)/0.05=2.0-2.6 (1-D RANGE model),

where the numerators and denominators of fractions are the $ODP(CH_3CCl_3)$ and $ODP(CHF_2Cl)$ respectively,estimated by the indicated models.

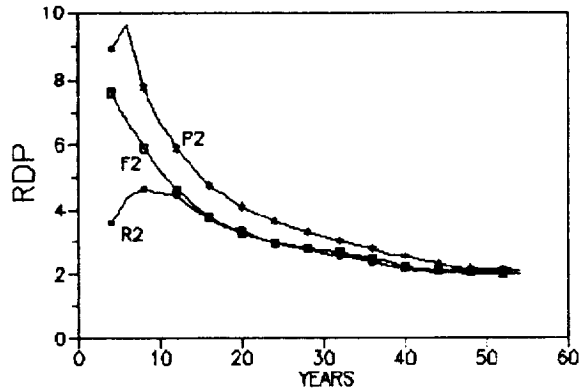

Fig. 2. The time dependence of RDP values for variants P2, R2 and F2 of Table 1.

The total ozone changes for variants R3 and FD3 are compared at the Fig.3. The start of calculations corresponds to 1985 and the years 1990 and 2000 of Fig.3 correspond to 5^{th} and 15^{th} model years and so on. According to the Fig.3, during the first 10-25 years the total ozone changes in steady state variant R3 exceed significantly the same changes of transient "dynamic" variant FD3: in the maximum peak the difference is about 10 D.U. But after the $25-30^{th}$ model year (2000-2010 in Fig.3) the total ozone changes of FD3 are bigger than the corresponding ones of R3, because of the chlorine atom flow intensity (in the CFCs and HCFCs) in variant FD3 exceed the "conserved" background chlorine content in the stratosphere of the steady state variant R3. Besides that in the first of them the shares of ozone active chlorine radicals (Cl and ClO) are higher and of passive compounds (HCl, HOCl) are lower than in the second variant in the middle and upper stratosphere. The RDP for FD3 variant is in about 1.5 times bigger than for R3 variant all the time and it is equal 3.77 for the year 2050.

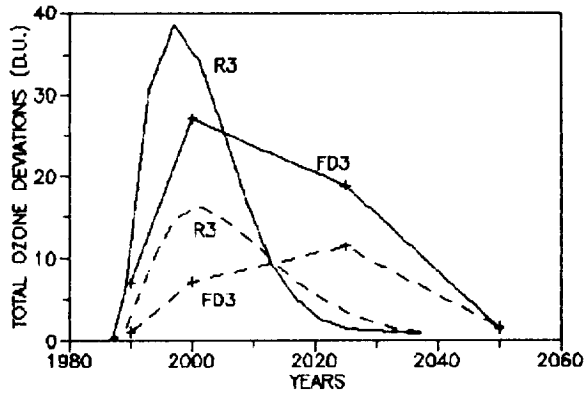

Fig. 3. The total ozone deviations of variants R3 and FD3 of Table 1 for CH_3CCl_3 (solid lines) and for CHF_2Cl (dashed lines).

The calculated lifetimes CH_3CCl_3 and CHF_2Cl for various variants are presented in the Table 3.

Table 3. The lifetimes τ of CH_3CCl_3 and CHF_2Cl (years) and RCLP values (see Text).

Variant	$\tau(CH_3CCl_3)$	$\tau(CHF_2Cl)$	RCLP
P2	9	20	0.87
R1	6-7	15	0.78-0.90
R2	5.5-6	15	0.71-0.78
R3	6-7	15	0.78-0.90
R4	5.5-6.5	13-14	0.76-0.97
F2	4-5	10-11	0.71-0.97

Here the lifetime of compound A is the period of the e time decrease of the initial A content. The tendency of the lifetime decrease for the transition to delayed initial background gas composition (i.e. from state P to state R and further to state F) occurs both for CH_3CCl_3 and CHF_2Cl. The obtained lifetimes are in quantitative agreement with their accepted values, which is equal to 6.3 years for CH_3CCl_3 and to 15-17 years for CHF_2Cl [WMO,1989; WMO/UNEP,1990].

Also the relative chlorine loading potentials of the ratio of CH_3CCl_3 and CHF_2Cl are estimated. The chlorine loading potential of compound A is defined in [WMO, 1989; WMO/UNEP,1991] as

$$CLP(A) = \frac{\tau(A)}{\tau(CFC\text{-}11)} \cdot \frac{M(CFC\text{-}11)}{M(A)} \cdot \frac{n(A)}{n(CFC\text{-}11)},$$

where τ, M and n are the lifetime, the molecular weight and the number of chlorine atoms per molecule in compound A or CFC-11 correspondingly. Then the ratio of the CH_3CCl_3 and CHF_2Cl chlorine loading potentials is

$$RCLP = \frac{CLP(CH_3CCl_3)}{CLP(CHF_2Cl)} = \frac{\tau(CH_3CCl_3)}{\tau(CHF_2Cl)} \cdot \frac{M(CHF_2Cl)}{M(CH_3CCl_3)} \cdot \frac{n(CH_3CCl_3)}{n(CHF_2Cl)} = 1.944 \cdot \frac{\tau(CH_3CCl_3)}{\tau(CHF_2Cl)},$$

because of values $M(CH_3CCl_3)=133.5$, $M(CHF_2Cl)=86.5$, $n(CH_3CCl_3)=3$ and $n(CHF_2Cl)=1$. The calculated RCLP values in Table 3 are somewhat higher than the corresponding values of other models: RCLP=0.67 (2-D OSLO model), RCLP=0.71 (2-D LLNL model), RCLP=0.62 (2-D AER model), RCLP=0.65 (DuPont), RCLP=0.67 (Solomon,Garcia) [S.Solomon et al., (1992)].

3. SUMMARY AND CONCLUSIONS

The ratio of ODPs and ODPs themselves depend significantly on the mass of the investigated compound release. The ratio of full ODPs slightly depends on initial background gas composition as the total ozone significantly decreases for delayed in time background atmospheric gas composition. This decrease is due to chronological increase (from period P to period F) of Cl_y content in the stratosphere. The background trace gases emission evolution leads to the significant changes of total ozone deviations in time and to RDP transient variant increase in comparison to stationary F3 variant. The large uncertainties in expected trace gases release scenarios requires the caution in application of these results. The lifetimes of CH_3CCl_3 and CHF_2Cl have the tendency to decrease for more anthropogenically loaded background gas composition (because of the OH content changes).

The obtained RDP values have a range about 30-50% for different conditions of the experiment, but this range may be somewhat bigger for other compounds. The obtained results have qualitative character and serve as the base for the further investigations only.

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